

STUDIES OF SOME COORDINATION COMPOUNDS
OF PLATINUM AND CHROMIUM

I. THE STRUCTURE OF PLATINUM-OLEFIN
COMPOUNDS

II. STUDIES IN THE CHROMAMMINES

BY

ALFRED LESTER OPPEGARD

A.B., Grinnell College, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN
CHEMISTRY IN THE GRADUATE SCHOOL OF
THE UNIVERSITY OF ILLINOIS, 1946

URBANA, ILLINOIS

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PART I. THE STRUCTURE OF PLATINUM-OLEFIN COMPOUNDS

The nature of the coordinate bond between olefinic substances and various metallic salts has aroused much speculation. Although these compounds bear many similarities to other coordination compounds the absence of an unshared pair of electrons in the coordinating groups contrasts sharply with the usual structure of a group which is capable of complexing with a metallic ion. It is for this reason that many investigators have speculated as to the mechanism of the bond formation in this class of compounds.¹

On the basis of experimental evidence gathered in the course of this research and by other investigators it is proposed that platinum-olefin complexes are formed by a bond between the platinum atom and the double bond of the olefin. Such a bond is similar to the protonated double bond proposed by Pitzer.² The platinated double bond is postulated to have the following properties:

- a. The double bond distance is increased to roughly that of a single bond.
- b. The double bond is not weakened to the extent that free rotation becomes possible.
- c. The double bond may be able to resonate with other conjugated double bonds.
- d. The olefin occupies one coordination position.
- e. The platinous platinum is in the customary dsp^2 state.

A similar sort of bond has been proposed for silver-olefin complexes by Winstein and Lucas.³ The platinated double bond is characterized by its greater stability.

Consideration of the molecular structure of $[PtCl_2.Un]_2$ in terms of the platinated double bond leads to the conclusion that the structure which Pfeiffer⁴ proposed is entirely satisfactory, $\begin{array}{ccc} Cl & Cl & Un. \\ Pt & Pt & \\ Un & Cl & Cl \end{array}$. Three geometrical isomers are possi-

ble, one in which two olefins are attached to one platinum, and

two in the event that each platinum has one olefin attached to it. The latter two are the most probable structures and a study of dipole moments should be of help in ascribing the true structure. Optical activity is also possible if an unsubstituted olefin such as styrene is used.

The infrared absorption spectra* have been determined for the following platinum-olefin complexes of the type $[\text{PtCl}_2.\text{Un}]_2$ where Un represents *trans*-stilbene, styrene, cyclohexene, ethylene, *cis*- and *trans*-2 pentene. The spectra of the olefins were also determined. In no instance are the spectra of the olefin and the complex derived from it alike. In no instance with the possible exception of *trans*-2-pentene is the characteristic $\text{C}=\text{C}$ absorption band in the region $1660\text{-}1620\text{ cm}^{-1}$ observed in the spectra of the complexes. A rigid structure is indicated by the differences in the spectra of the complexes of *cis*- and *trans*-2-pentene. It is concluded from these data that the double bond disappears upon complex formation, yet a rigid structure is maintained which does not permit *cis-trans*-rearrangements.

Molecular weight determinations in benzene solution indicate that $[\text{PtCl}_2.\text{C}_2\text{H}_4.\text{quinoline}]$ and $[\text{PtCl}_2.\text{styrene quinoline}]$ are monomeric. It is concluded from this that each olefin is attached to only one platinum atom, and that each olefin probably occupies only one coordination position.

Ultraviolet absorption spectra of $[\text{PtCl}_2.\text{styrene}]_2$, $[\text{PtCl}_2.\text{trans-stilbene}]_2$, and $[\text{PtCl}_2.1\text{-pentene}]_2$ do not clearly indicate whether a double bond which is coordinated to a platinum atom can resonate with other conjugated double bonds.

The method of continuous variations⁵ has been applied to a study of the reactions of maleic and fumaric acids with potassium chloroplatinite. Maleic acid reacts with potassium chloroplatinite in aqueous solution in a 1:1 ratio to form $\text{K}[\text{PtCl}_3.\text{maleic acid}]$. Fumaric acid causes some reduction of the chloroplatinite to metallic platinum. The colloidal platinum thus formed obscures any complex formation which may take place.

*Mrs. Agatha Johnson is to be thanked for determining the infrared spectra.

PART II. STUDIES IN THE CHROMAMMINES

The growing importance of the complex compounds of chromium has focused attention upon the methods of preparations which are available. While many of the methods are satisfactory for the preparation of small amounts, the manufacture of these materials on a large scale demands more simplified procedures. Furthermore, the starting materials specified in many procedures are in themselves difficult to prepare, thereby complicating the picture.

A survey has been made of the properties and methods of preparation of three common coordination compounds of chromium and new or improved methods of synthesis developed for two of them.

Chloropentammino Chromic Chloride, $[\text{Cr}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

The reaction of anhydrous chromic chloride with liquid ammonia to produce chloropentammino chromic chloride and hexammino chromic chloride⁶ is satisfactory except that two products are formed and anhydrous chromic chloride is expensive. The preparation of anhydrous rare earth chlorides by dehydration of the hydrated chloride in the presence of ammonium chloride⁷ suggested the possibility of preparing anhydrous chromic chloride in the same manner. It is not possible to prepare anhydrous chromic chloride in such a fashion but the product which is obtained reacts with liquid ammonia to form chloropentammino chromic chloride in 38 per cent yield based on hydrated chromic chloride. The dehydration of chromic chloride hexahydrate can be accomplished at 110° C. in the presence of three moles of ammonium chloride. The theoretical amount of water is lost, yielding a product which is soluble in water and has a bright violet color.

Hexammino Chromic Nitrate, $[\text{Cr}(\text{NH}_3)_6](\text{NO}_3)_3$

Rollinson⁸ found that chloropentammino chromic chloride was one of the products of the reaction between anhydrous chromic chloride and liquid ammonia because chloropentammino chromic chloride is insoluble in liquid ammonia. However, chloropentammino chromic nitrate is soluble in liquid ammonia and

can be readily ammonated to the hexammine in the presence of a little sodamide. This suggested using sodamide as a catalyst in the reaction of liquid ammonia with anhydrous chromic chloride. In the presence of sodamide a 95 per cent yield of hexamino chromic nitrate can be prepared.

Thiocyanatoammino Chromic Chlorides.

Attempts to prepare thiocyanatoammino chromic compounds by the reaction of anhydrous chromic chloride with liquid ammonia in the presence of potassium or ammonium thiocyanate were unsuccessful.

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VITA

The author was born in Beloit, Wisconsin on April 13, 1920. He attended the public schools of Chicago, Illinois, and was graduated from the Carl Schurz High School in 1937. After receiving the Degree of Associate in Arts from North Park Junior College in 1939 he enrolled in Grinnell College, receiving the Degree of Bachelor of Arts in 1941. He entered the Graduate School of the University of Illinois and held a teaching assistantship for the year 1941-42. The following year he was awarded a Henry Strong Fellowship which he resigned in February, 1943, in order to participate in the Rubber Research Program sponsored by the War Production Board at the University of Illinois. With the exception of a leave of absence from January to June, 1944, to do research work under contract to Picatinny Arsenal he remained on the Rubber Research Program until February, 1946. At this time he was awarded a Standard Oil (Indiana) Fellowship for the period February to August, 1946.

The author is a member of the American Chemical Society, Sigma Xi, Phi Beta Kappa, Phi Lambda Upsilon and Phi Theta Kappa.



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